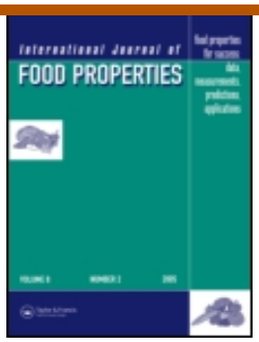

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ANALYSIS OF BLACK MULBERRY VOLATILES USING GCxGC-TOF/MS

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Volatile constituents of black mulberry (*Morus nigra*) dried with various commercially used techniques (sun, hot air, and microwaves) were obtained by direct thermal desorption and analysed using comprehensive GCxGC coupled with time of flight mass spectrometry (TOF/MS). Some mulberries were dried using only a desiccator and the volatile desorbed from these was used for comparison. The number of components of volatile fractions obtained for the desiccator, sun, microwave and hot air dried samples were 45, 43, 41, and 40, respectively. Acetic acid (8.18%), ethyl linolenate (7.43%), hexanol (5.42%), 3-methylbutanal (5.01%), 2,3-butanediol (4.93%), 3-hydroxy-2-butanone (4.82%), and 2,3-pentanedione (4.18%) were found to be the major components in the desiccator-dried samples. The profiles of the volatiles desorbed changed when other drying techniques (sun, hot air, and microwaves) were used. Isobutanal, pentanal, 1,2-propanediol, octane, and linalool acetate were found only in the desiccator-dried mulberry samples.

Keywords: ***Mulberry, Direct thermal desorption, Volatiles, Drying, GCxGC-TOF/MS.***

INTRODUCTION

Black mulberry is a very appealing fruit, but its soft flesh makes it difficult to transport as a fresh fruit. It is mostly processed into syrups to make cold drinks and into jams. It is also common in the eastern part of Turkey to process it into the dried form for consumption as a snack. Volatiles are known to affect the sensorial quality of both fresh and processed fruits. The concentration of fruit volatiles can be affected by processing conditions as well as agronomic factors.[1] There have been some studies done on the volatile components of various fruits.[1,2] There are few studies on the volatile components of various varieties of berries.[3,4] There is also one study on the flavour components of black mulberry (*Morus nigra*).[5] However, they have characterised only the flavour components of fresh mulberry, and there is scarcely any data found in the literature on the volatiles of dried mulberry.

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Drying is the most important process in the successful storage of fruits and vegetables. Though sun drying is the most common method employed, it is time consuming and prone to contamination with dust and insects, aside from being weather dependent. Microwave drying and hot air drying methods are also used. When a wet solid is exposed to microwave heating, its temperature may reach the boiling point of the liquid it contains. This process leads to very rapid drying without overheating the atmosphere or the surface in comparison to hot air drying. Mulberries at the time of harvest have a moisture content of 80–85% (wet basis).

The analysis of volatiles is generally accomplished by an extraction step, followed by concentration, chromatographic separation, and subsequent detection. An overview of sample preparation methods is provided by Pillonel et al.[6] for food volatiles and by Wilkes et al.[7] for food flavours and off-flavours. The chromatographic profile will vary depending upon the method of sample preparation employed, and it is not uncommon to produce artifacts during this step. Direct thermal desorption (DTD) is one version of a dynamic headspace technique with cryogenic trapping post desorption used to enrich the analytes prior to separation. DTD has important advantages over the other methods such as the ability to be directly coupled to gas chromatography-mass spectrometry,[8] the requirement of only a small amount of sample, and of course, the fact that it is a rapid method. It is suitable especially for rapid qualitative compound analysis. Comprehensive gas chromatography (GCxGC) is a multi-dimensional GC technique that has an increased separation power with reduced analysis time. The number of satisfactorily resolved peaks is much larger in GCxGC than in one dimensional GC. Also the limit of detection is 3 to 5 times better than GC when GCxGC is used.[9] The main objective of this study has been to examine the effect of different drying techniques on the volatile components of black mulberry using DTD coupled with GCxGC-TOF/MS.

MATERIALS AND METHODS

Materials

Black mulberries (*M. nigra*) were harvested by hand from the same tree nearby a village in Gaziantep, Turkey. The berries were dried on the day of harvest, using either the sun or hot air, microwaves or a desiccator. The initial moisture content of the mulberries was 80.12% (wet basis).

Drying Methods

Sun drying was achieved by spreading the mulberry samples on cloth for 3 days under the effect of the sun's rays. The samples dried to a moisture content of 15% wet basis, which is the level of drying normally used in commercial production. Hot air drying was performed in a pilot plant tray dryer (UOP 8 Tray dryer, Armfield Ltd, UK), which was operated at an air velocity of 1.5 m s^{-1} at a temperature of 80°C. The drying process took 450 min to reach a moisture content of 15% wet basis.

For microwave drying, a programmable domestic microwave oven (Arçelik ARMD 580, Turkey), with a maximum output of 700 W at 2450 MHz was used. A power level of 70 W was used after a few trials to dry the product used in this study. The drying process was ended after 100 min when the material had reached a moisture content of 15% wet basis. Some mulberries were dried using only a desiccator. This was done so that the

resulting desorbed volatile could be used for comparison since with the low temperature applied and less severe conditions, the desiccator-only dried samples were thought to be most alike fresh ones. The samples to be dried in the desiccator were divided into very small pieces. The divided pieces were placed in a glass desiccator, which contained PCl_5 at the bottom. The glass desiccator was flushed with nitrogen gas and stored in the dark at 5°C until the mulberry samples were dried to below 5% moisture content. Maximum drying time in the desiccator was 72 h.

For direct thermal desorption, samples of very low water content are necessary. The samples dried by the commercial methods of sun, hot air, and microwaves would be too high in water content at 15% wet basis. Further drying was therefore needed and to avoid any deleterious effects of further drying by these three methods, these samples were further dried in the desiccator to below 5% wet basis, undergoing the same process in the desiccator as described above. All mulberry samples were kept in polyethylene bags at 5°C until analyzed.

Direct Thermal Desorption

A GCXGC-TOF/MS system was used together with a dual stage commercial thermal desorption injector. This incorporated a thermal desorption unit (TDU) connected to a programmable-temperature vaporisation (PTV) injector, CIS-4 plus (Gerstel, Mulheim an der Ruhr, Germany), using a heated transfer line. The injector was equipped with a MPS autosampler (Gerstel). Empty glass thermodesorption tubes were conditioned at 400°C for 2 h prior to each use. 2–5 mg quantities of dried sample (from which the seeds had been removed) were placed in thermodesorption tubes using tweezers to ensure no contamination of the sample. Glass wool was used to hold the sample in place.

Initial desorption was carried out at 125°C using the TDU for three minutes under a helium flow of 1.5 mL min^{-1} in the splitless mode while maintaining a cryofocussing temperature of 20°C in the PTV injector of the GC–MS system. After cooling of the TDU to 40°C, the programmable temperature vaporisation system was ramped to a final temperature of 200°C and the analytes were transferred to the GC column.

Chromatographic Analysis

The GCxGC–TOF/MS system consisted of an HP 6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph and a Pegasus III TOF-MS (LECO, St. Joseph, MI, USA). The first column was a non-polar DB5 (28.8 m × 0.32 mm i.d. × 0.25 μm film thickness) and the second column a DB17 (2.1 m × 0.10 mm i.d. × 0.10 μm film thickness). Both columns were purchased from J & W Scientific (Folsom, CA, USA). The columns were connected by means of a press-fit-connector. The second dimension column was installed in a separate oven, which was maintained in the main GC oven. The separate oven provided a more flexible system since it allows fine-tuning of the retention in the second column by using a higher or lower temperature relative to the first dimension column. In this particular system, the need to use a two-oven system was driven by detector stability considerations, requiring accurate and stable control of the second column's temperature. This temperature control of both ovens enables more rapid and higher resolution separations.

The modulator is the key to the performance of the GCxGC experiment. In this case we used cryogenic modulation performed using a jet-type modulator installed at the head

of the second dimension column. It consisted of two cold and two hot jets, with the nozzles providing the cold jets mounted orthogonal to the hot jets. Nitrogen gas was cooled by heat exchange through copper tubing immersed in liquid nitrogen outside the GC system and delivered through vacuum-insulated tubing to the cold jets, which provide two continuous jets of approximately 10 L min^{-1} of cold nitrogen gas at approximately −140°C. Three modulation periods were used (6, 8, 10 s). When the hot downstream pulse is fired the analytes are effectively injected into the second dimension column.

Helium was used as a carrier gas. The initial temperature of the first dimension column was 60°C for 30 s and the subsequent temperature programme was a heating rate of 5°C min^{-1} until 280°C was reached and held isothermally for a further 2 min. The initial temperature of the second dimension column was 75°C for 30 s and a 5°C min^{-1} heating rate was used until 300°C was reached and held isothermally for further 2 min. Peak identification was made using TOF/MS with electron impact ionisation. The mass spectrometer used a push plate frequency of 5 kHz, with transient spectra averaging to give unit resolved mass spectra between 45 and 350 amu at a rate of 50 spectra s^{-1}. Mass spectra were compared against the NIST mass spectral library.

Statistical Analysis

Results are the means of four experiments ($N = 4$). An ANOVA was performed for each component as a function of drying method to determine significant differences ($P < 0.05$) using SPSS version 16.0 (SPSS Inc., Chicago, IL, USA). Duncan's multiple range test was also carried out for each component for determination of homogeneous groups using SPSS version 16.0.

RESULTS AND DİSCUSSİON

The volatile components of black mulberry dried by different techniques (desiccator, sun, microwave, and hot air) were isolated using the direct thermal desorption technique with a cryofocusing trap and analysed by GCxGC-TOF/MS. As it has been discussed by Grimm et al.,[10] sample preparation is the crucial step for the further analysis of compounds. Pillonel et al.[6] described some of the advantages of the thermal desorption techniques as follows: (i) analysis of 100% of the trap content (instead of an aliquot part), (ii) no solvent peak, (iii) no waste, and (iv) no contamination. The optimisation of the DTD temperature for plant materials[11] has been studied previously and 150°C was found to be the best from the 100–250°C range studied. However, lower direct thermal desorption temperatures (100, 125, 150°C) for desiccator dried samples have been studied to eliminate the possible risk of browning reactions with the high sugar content of mulberries. It has been found in these preliminary studies that 125°C was better compared to 100°C in extracting all the volatiles and better than 150°C in eliminating the browning reactions products. The DTD temperature used, therefore, was 125°C in this study. The time of thermal desorption was 3 min at this temperature. The volatile constituents of the apricot samples obtained from this were immediately analysed using in-line GCxGC-TOF/MS.

Table 1 lists the compounds identified in the volatiles of dried mulberry samples using DTD together with their Kovats indices, corresponding percentage compositions and their standard deviations. It should be noted that the peak identification of components is based on both library mass spectra and Kovats indices. Identification was based on a mass

spectral library search using similarity and reverse factors above 750 and 800, respectively. Lower values than these were counted as unknown and components having these low values were not compared for their Kovats indices. Mass spectral match factors (similarity and reverse factors) are often much higher for GCxGC compared with conventional one-dimensional GC due to better separation of components.[9] Özel et al.[11] and Dalluge et al.[12] also used similarity and reverse factors above 750 and 800, respectively.

Table 1 Compounds, retention indices and percentage compositions of the volatiles of black mulberry (*Morus nigra*) samples produced using various drying techniques.

Compound[1]	RI[2]	Desiccator (%)[3]	Sun (%)[3]	Microwave (%)[3]	Hot air (%)[3]
Propanal	506	0.73 ± 0.06[4] a	0.32 ± 0.08 b	0.14 ± 0.05 b	0.14 ± 0.05 b
Isobutanal	540	1.01 ± 0.09 a	–[5]	–	–
2,3-Butanedione	593	3.48 ± 0.35 a	3.43 ± 0.56 a	2.27 ± 0.12 a	2.42 ± 0.42 a
Acetic acid	600	8.18 ± 0.82 a	8.98 ± 0.77 a	7.12 ± 0.35 a	8.07 ± 0.66 a
Ethyl acetate	628	1.91 ± 0.13 a	1.06 ± 0.43 ab	0.87 ± 0.09 b	0.64 ± 0.08 b
3-Methylbutanal	641	5.01 ± 0.47 a	5.01 ± 0.56 a	4.67 ± 0.26 a	4.65 ± 0.71 a
Ethanol	668	2.36 ± 0.16 a	2.18 ± 0.49 a	1.06 ± 0.31 ab	0.95 ± 0.18 b
2,3-Pentanedione	701	4.18 ± 0.42 a	3.71 ± 0.28 a	2.82 ± 0.45 a	3.36 ± 0.27 a
3-Hydroxy-2-butanone	718	4.82 ± 0.29 a	5.36 ± 0.85 a	1.38 ± 0.19 b	1.92 ± 0.19 b
Pentanal	732	2.08 ± 0.36 a	–	–	–
1,2-propanediol	792	1.01 ± 0.10 a	–	–	–
Octane	800	0.44 ± 0.08 a	–	–	–
Hexanal	801	0.95 ± 0.11 a	0.47 ± 0.09 b	0.31 ± 0.05 b	0.97 ± 0.08 a
2,3-Butanediol	806	4.93 ± 0.34 a	4.56 ± 0.87 a	4.37 ± 0.25 a	4.07 ± 0.37 a
Butyl acetate	816	2.59 ± 0.45 a	1.48 ± 0.38 ab	1.76 ± 0.27 ab	0.86 ± 0.09 b
Furfural	829	–	2.68 ± 0.57 a	3.64 ± 0.36 a	4.20 ± 0.25 a
Hexanol	851	5.42 ± 0.56 a	2.18 ± 0.29 b	1.28 ± 0.26 b	1.98 ± 0.35 b
Heptanal	903	0.18 ± 0.03 a	0.23 ± 0.08 a	0.10 ± 0.05 a	–
5-Methylfurfural	978	0.93 ± 0.12 d	4.13 ± 0.35 c	10.49 ± 0.86 a	7.30 ± 0.43 b
Octanol	981	6.76 ± 0.43 a	5.28 ± 0.61 ab	3.75 ± 0.39 b	3.98 ± 0.47 b
Octanal	1003	0.49 ± 0.11 a	0.17 ± 0.07 b	0.15 ± 0.05 b	0.11 ± 0.04 b
2-Ethylhexanol	1032	0.09 ± 0.04 a	0.19 ± 0.05 a	0.10 ± 0.04 a	0.15 ± 0.08 a
Dimethylmethoxyfuranone	1049	–	0.92 ± 0.17 a	0.49 ± 0.08 a	0.87 ± 0.13 a
Hexanoic acid	1089	0.43 ± 0.07 a	0.58 ± 0.07 a	0.19 ± 0.07 a	0.51 ± 0.21 a
Nonanal	1103	0.94 ± 0.11 b	1.59 ± 0.19 a	0.39 ± 0.09 c	0.42 ± 0.09 c
Heptanoic acid	1112	0.10 ± 0.02 a	0.12 ± 0.06 a	0.18 ± 0.05 a	0.11 ± 0.04 a
2-Phenylethyl Alcohol	1118	0.37 ± 0.08 a	0.16 ± 0.08 a	0.13 ± 0.06 a	0.14 ± 0.05 a
Nonanol	1159	3.68 ± 0.34 a	2.25 ± 0.42 b	2.17 ± 0.32 b	2.05 ± 0.29 b
Decanal	1209	0.10 ± 0.03 a	0.28 ± 0.09 a	0.32 ± 0.08 a	0.20 ± 0.06 a
5-HMF	1241	0.84 ± 0.09 c	9.42 ± 0.71 b	19.54 ± 1.85 a	16.73 ± 2.13 a
Neral	1247	3.71 ± 0.46 a	3.75 ± 0.48 a	3.12 ± 0.46 a	2.45 ± 0.44 a
Linalool acetate	1264	0.52 ± 0.08 a	–	–	–
Nonanoic acid	1275	0.44 ± 0.11 ab	0.64 ± 0.11 ab	0.39 ± 0.13 b	0.98 ± 0.18 a
Geranial	1277	3.65 ± 0.49 a	3.39 ± 0.45 a	3.17 ± 0.28 a	3.12 ± 0.27 a
Octanoic Acid	1279	0.24 ± 0.10 a	0.36 ± 0.08 a	0.37 ± 0.11 a	0.27 ± 0.05 a
Butyrolactone	1299	2.35 ± 0.51 a	1.54 ± 0.29 ab	0.52 ± 0.08 b	0.59 ± 0.09 b
Decanoic acid	1373	0.10 ± 0.05 a	0.27 ± 0.06 a	0.13 ± 0.04 a	0.11 ± 0.04 a
Caryohyllene	1426	1.32 ± 0.27 a	0.85 ± 0.11 a	0.96 ± 0.07 a	0.88 ± 0.12 a
Germacrene-D	1482	0.45 ± 0.13 a	0.23 ± 0.05 a	–	–
γ-Elemene	1490	0.51 ± 0.08 a	0.34 ± 0.08 a	–	–
Dibutyl phthalate	1968	1.66 ± 0.26 b	1.04 ± 0.19 bc	0.46 ± 0.08 c	2.37 ± 0.25 ab
Ethyl palmitate	1993	1.22 ± 0.33 a	1.64 ± 0.15 a	1.16 ± 0.09 a	1.38 ± 0.31 a

(*Continued*)

Table 1 (Continued)

Compound[1]	RI[2]	Desiccator (%)[3]	Sun (%)[3]	Microwave (%)[3]	Hot air (%)[3]
Methyl linolenate	2092	3.94 ± 0.46 a	3.24 ± 0.26 a	3.48 ± 0.27 a	3.11 ± 0.44 a
Octadecadienoic acid	2094	3.90 ± 0.48 a	3.61 ± 0.32 a	3.20 ± 0.25 a	3.41 ± 0.29 a
Octadecenoic acid	2102	–	0.23 ± 0.09 a	0.27 ± 0.08 a	0.27 ± 0.05 a
Tetradecanoic acid	2140	0.50 ± 0.07 a	0.10 ± 0.05 b	0.11 ± 0.04 b	0.11 ± 0.04 b
Ethyl linolenate	2171	7.43 ± 0.55 a	6.43 ± 0.31 a	6.35 ± 0.36 a	6.18 ± 0.27 a
Hexadecanoic acid	2380	0.10 ± 0.05 c	0.17 ± 0.05 c	1.05 ± 0.29 b	1.90 ± 0.31 a
Unknown		3.94 ± 0.46 a	5.39 ± 0.39 a	5.54 ± 0.65 a	6.05 ± 0.81 a
Total compounds		45	43	41	40

Different letters indicate a statistical difference at the $\alpha = 0.05$ level in each row. RI: Retention index.[1] As identified by GC-TOF/MS software; names according to NIST mass spectral library, and by comparing their Kovats retention indices.[2] Kovats retention indices of each component was collected from the literature for column DB5.[3] Percentage of each component is calculated as peak area of analyte divided by peak area of total ion chromatogram times 100 (In the case of multiple identification, the areas of the peaks that belong to one analyte were combined to find the total area for this particular analyte);[4] the standard deviations for four (N = 4) experiments; and[5] not detected or percentage of the component is lower than 0.05%.

The samples dried only in the desiccator at 5°C were prepared to represent the volatile constituents of the fresh mulberry to use for comparison. A range of alcohols (24.62%), esters (19.27%), aldehydes (18.85%), acids (14.00%), ketones (12.48%), hydrocarbons (2.72%), and lactone (2.35%) were found to be present in its volatiles. The major components identified in the desiccator dried mulberry were acetic acid (8.18%), ethyl linolenate (7.43%), hexanol (5.42%), 3-methylbutanal (5.01%), 2,3-butanediol (4.93%), 3-hydroxy-2-butanone (4.82%), and 2,3-pentanedione (4.18%). The overall number of compounds found for the desiccator-dried mulberries was found to be 42. Qian and Wang[4] reported a similar alcohol content (21.94%) for blackberry volatiles. In our study, we found the total percentage of fatty acids to be 5.81%. However, previous studies of the volatile compounds of black mulberry found somewhat different results: the majority of the compounds were fatty acids and their esters.[5] They reported that the overall number of extracted flavouring compounds for three different varieties of black mulberries studied was 18. These differences could be because the present study did not include seeds in the samples. It should also be noted that the extraction techniques were different in these studies and DTD as a sample preparation technique is quite advantageous over the other methods.[13]

It was noted that the method of drying the mulberry samples resulted in a change in compositions of their volatiles. The number of components of volatile fractions obtained for the desiccator, sun, microwave and hot air dried samples was 45, 43, 41, and 40, respectively. Components having a percentage of less than 0.05%, even if identified by GC-TOF/MS, are not shown in this paper. The number of identified components common to all mulberry samples was 37. Isobutanal, pentanal, 1,2-propanediol, octane and linalool acetate were found only in the desiccator dried mulberry samples and disappeared completely with the application of the other drying techniques. Elmacı and Altuğ[5] reported that ethyl linolenate was found to have a note which is unique for black mulberry flavour. A significant percentage of ethyl linolenate (7.43%) was found in desiccator dried mulberries in the present study. It is also important to note that the percentage of ethyl linolenate did not change significantly ($P < 0.05$) with the different methods of drying.

The major volatile components of mulberry changed drastically when dried by commercial techniques (sun, hot air, and microwaves). The main components identified

using these drying techniques were acetic acid, 5-hydroxymethylfurfural (5-HMF) and 5-methylfurfural. 5-HMF and 5-methylfurfural together with other minor ones (furfural and dimethylmethoxyfuranone) are known to be the result of browning reactions. Furaneol and 5-methyl furfural have also been found as Maillard reaction products in dried prunes[14] and 5-HMF in sultana grapes.[15] It is known that the heat treatment of fruits and vegetables often reduces the number of original volatile flavour compounds, whilst at the same time, introducing additional ones through the autoxidation of unsaturated fatty acids, decomposition of amino acids and thermal decomposition and/or initiation of caramelisation and/or Maillard reactions. Maillard reaction products may negatively affect the flavour of the dried product. Black mulberry is very low in fat (0.95%) and high in sugar content (total soluble solids, 16.7%).[16] This composition makes it sensitive to browning reactions especially during drying. The browning reaction products were only 1.77% in the desiccator dried mulberry samples. However, they were 17.15, 34.16, and 29.10% for the sun, microwave and hot air dried samples of mulberry, respectively. There is no quantitative data given in this study to compare the percentage retention of the volatiles between fresh and dried samples.

Over 90% of the volatiles defined were the same whether sun, hot air, or microwave drying had been used. However, hot air and microwave drying made a difference to the volatile profiles. For example, 5-methyl furfural and 5-HMF increased drastically in the hot air and microwave dried samples. However, the percentage concentrations of ethanol, hexanol, octanol, and butyrolactone showed a significant decline. Lunning et al.,[17] studied how hot air drying at 65°C affected the amount of volatile compounds found in peppers. They also found that some of the components (β-ocimene, hexanol, 3-hexenol, and heptyl 6-methyl-2-propenoate) had declined considerably. Among the three commercial techniques studied, sun drying was found to be best in that fewer degradation products were produced and the components of its resulting volatile were more alike that of the desiccator-only dried sample.

CONCLUSIONS

In this study, DTD coupled with GCxGC-TOF/MS was used to study volatile constituents of dried black mulberry. It is a viable technique for use in industry to monitor the quality of the drying process of mulberries. Samples could be rapidly and easily analyzed without the need for costly and time-consuming sample preparation stages. Batches of dried mulberries could be analyzed to check their levels of degradation products. It was found that the number of components extracted at a desorption temperature of 125°C were 45, 43, 41, and 40 for the desiccator, sun, microwave and hot air dried samples respectively. The major components of the volatiles changed with the various drying techniques. Among the three commercial techniques studied, sun drying was found to be best in that fewer degradation products were produced and the components of its resulting volatile were more alike that of the dessicator-only dried sample.

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